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Introduction

Acid ferric sulfate solution has been used for heap and dump leaching of low-grade chalcopyrite ores and is being considered as a possible lixiviant for the hydrometallurgical processing of copper sulfide concentrates. For many years, researchers have attempted to explain the leaching behavior of chalcopyrite, since the reaction rate kinetics are extremely slow and seem to be significantly influenced by the nature of the reaction product. A summary of conclusions drawn from reported literature on chalcopyrite leaching is found in the paper by Munoz, Miller, and Wadsworth[1] and more recently by Dutrizac.[2] Lowe[3] and Jones and Peters[4] attributed rate control to a surface reaction. Linge,[5] Dutrizac,[6] Bauer,[7] and researchers at the University of Utah[1,8] reported that the reaction rate is limited by transport in the chalcopyrite lattice or through the elemental sulfur reaction product layer. Munoz et al.[1] presented a model, derived from the Wagner theory of oxidation, which is based on the formation of a protective sulfur layer with rate control by electron transport through the insulating sulfur layer. By utilizing Wagner's parabolic oxidation relationships,[9] the following equation was obtained:

$$\frac{d\alpha}{dt} = 300 \frac{3t_e \sigma \Delta G}{\rho_B d_o^2 e^2} \cdot \frac{(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}} \qquad (1)$$

where α is the fraction of $CuFeS_2$ reacted at time t, ρ_B is the molar density of $CuFeS_2$, d_o is the initial diameter of the particle, e is the electronic charge, $\dot{\sigma}$ is the total electrical conductivity of the sulfur layer, and ΔG is the Gibbs free energy for the reaction:

$$\frac{1}{4}\,CuFeS_2 + Fe^{3+} = \frac{1}{4}\,Cu^{2+} + \frac{5}{4}\,Fe^{2+} + \frac{1}{2}\,S^{o}$$

Miller and Portillo[10] modified the sulfur layer chemically by a modest addition of silver to the leaching system with a phenomenon increase in the leaching rate. Under these circumstances, it appears that the sulfur is no longer protective but forms a relatively porous reaction product layer compared to the smooth tenacious layer of elemental sulfur formed in the unactivated reaction.

If the reaction rate for ferric sulfate leaching of chalcopyrite is limited by electron transport in the protective elemental sulfur product layer, modification of this reaction product layer to increase its conductivity should increase the rate of the leaching reaction. To obtain an increase in the electrical conductivity of the sulfur layer, the principles of solid-state chemistry as applied to the conductivity of insulators and semiconductors may be considered.

In 1972 Wagner[11] presented the concept that the electrical conductivity of an insulator phase may be altered by the addition of dispersed particles in the insulator phase. The conductivity increase is due to the emission of electrons from the particles. With respect to the conductivity of elemental sulfur, investigators[12] have found that the addition of carbon particles to elemental sulfur can increase the electrical conductivity of liquid sulfur. Recently, Simkovich et al.[13] studied the electrical conductivity of C-S systems. They found that carbon addition (Black Pearl 2000) to elemental sulfur increased the electrical conductivity of the sulfur by about 12 orders of magnitude.

Assuming that carbon particles can be dispersed in the sulfur product layer and act in a similar manner, the ferric sulfate leaching of chalcopyrite would be expected to increase, at least until another step in the reaction sequence becomes rate determining. However, it can be imagined that the addition of such carbon particles may alter other physical-chemical properties such as the surface chemistry and the structural features or product morphology.

The objective of the current research is to accelerate the rate of the ferric sulfate leaching of chalcopyrite by alteration of the passivating sulfur product layer with the addition of particulate carbon. Further, the research effort is intended to define the mechanistic details of the effect of particulate carbon addition and how it relates to the results of previous investigations. Further discussion regarding the reaction mechanism for the enhanced ferric sulfate leaching of $CuFeS_2$/C composites will be presented at the "International Conference on Recent Advances in Mineral Science and Technology," South Africa, March 1984.[14]

Experimental

Experiments were designed to study the effects of particulate carbon additions on ferric sulfate leaching of chalcopyrite. To obtain contact between chalcopyrite and carbon particles, an experimental technique was used which involved intimate mixing of the particles and compression of the mixture to form a $CuFeS_2$/C pellet. Generally the pellet was broken into aggregates. The ferric sulfate leaching of $CuFeS_2$/C aggregates was carried out under atmospheric pressure. The reaction rates were followed by copper analysis of solution samples taken at timed intervals.

Materials

The chalcopyrite used in this research was obtained from a Pima flotation concentrate. Chemical and mineralogical analyses are shown in Table 1, provided by the U.S. Bureau of Mines, Salt Lake City Metallurgical Research Center.

Table 1. Analysis of Pima Concentrate as Received.

Chemical Analyses		Mineralogical	
Element	%	Mineral	%
Cu	27.2	$CuFeS_2$	80
Fe	29.2	FeS_2	5
S	20.8	SiO_2	5
Sb	0.60	Al_2O_3	1
Zn	0.50	CaO	1
Mo	0.14	Talc and chlorites	8
Pb	0.07		
As	0.02		

Monosize chalcopyrite samples were prepared from the concentrate by wet screening and sizing with a Warman Cyclosizer. Gangue minerals were separated from the monosize chalcopyrite samples with a Carpco Laboratory Model magnetic separator. The samples thus prepared have an exceptionally high purity. Also, a 5x2-micron monosize sample was prepared from the concentrate by the Donaldson Company with an Accucut Model B air classifier. The particle size distribution for each sample was determined with a Micromeritics Sedigraph Size Analyzer as shown in Figure 1.

Results of the chemical analysis of each monosize sample (characterized by the median size of their narrow size distribution) are shown in Table 2.

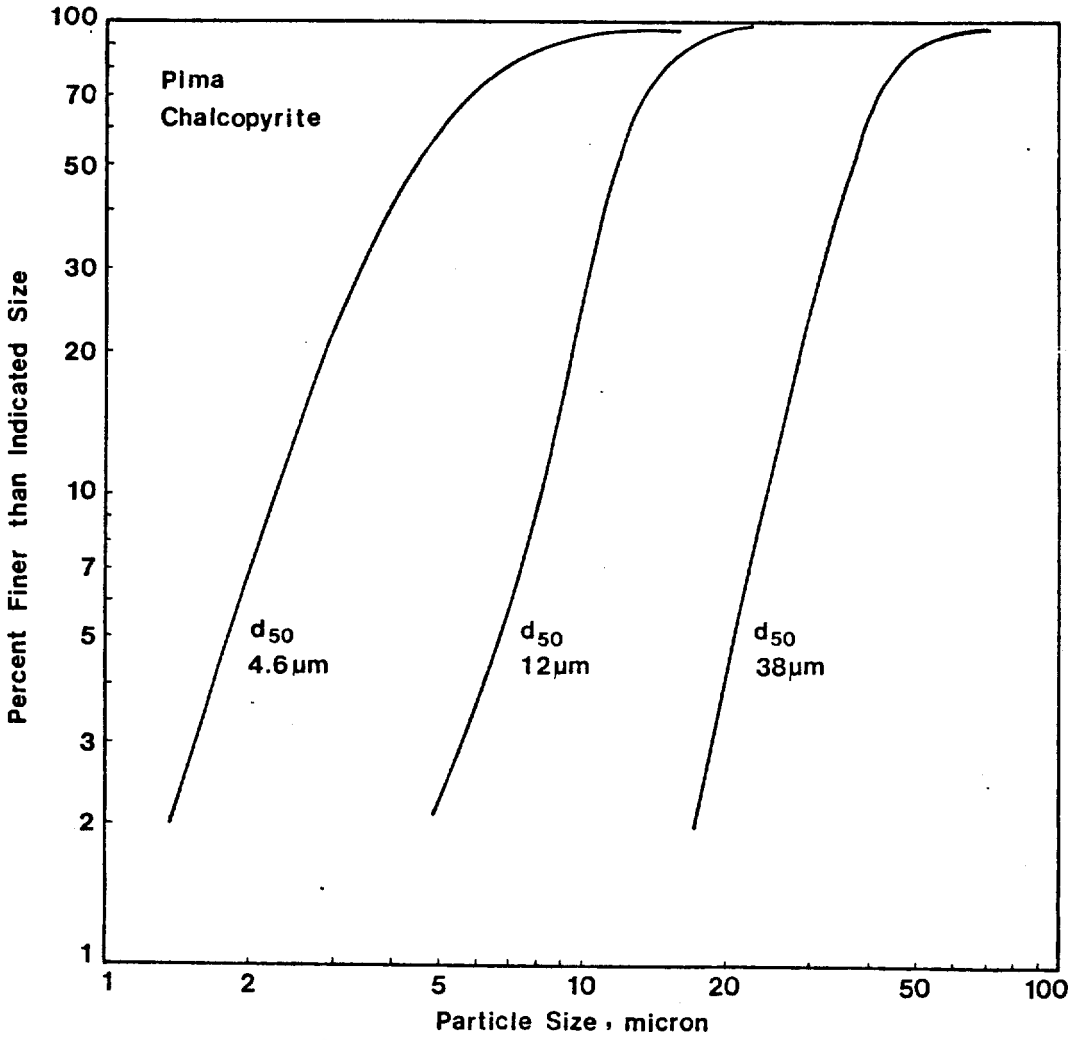

Figure 1. Size distribution of chalcopyrite samples as determined by Micromeritics Sedigraph Size Analyzer.

Table 2. Chemical Analysis for Prepared Monosize Chalcopyrite Samples.

d_{50} size (microns)	Chemical Analysis	
	Cu %	Fe %
4.6	29.95	26.27
12.0	30.49	26.85
28.0	30.75	27.25
38.0	31.58	27.73

Various carbons of high purity were obtained from the Cabot Carbon Corp., Fisher Scientific Company, Cerac Corp., Lonza Inc., and AESAR Inc. The particle size of carbon was determined by Coulter Counter Analysis. The surface areas were measured using the BET technique — Quantasorb made by Quantachrome Corporation.

Distilled water and reagent-grade chemicals were used to prepare the desired leaching solutions.

Apparatus and Procedure

Leaching Experiments. Chalcopyrite and carbon particles were mixed thoroughly and pressed into pellets of appropriate size. The diameter of the $CuFeS_2/C$ pellets was 1.3 cm, and the thickness of the pellets depended upon the amount of sample used. Most samples were 0.24 cm thick. The pellets were prepared at 20,000 lb. The compression and porosity of the pellet depend on the particle size and the proportion of chalcopyrite to carbon. Preparation of $CuFeS_2/C$ aggregates from 38-micron chalcopyrite particles results in significant breakage of these particles, particularly for small additions of carbon. Generally, $CuFeS_2/C$ aggregates prepared from fine chalcopyrite particles are more compact and exhibit greater structural integrity.

All leaching experiments were carried out in one-liter cylindrical reactors immersed in thermostatically controlled water baths. The baffled glass reactors had a clamp-held lid containing four fitted openings. A stirrer, fritted solution sampler, condenser, and thermometer were placed into the reactors through these openings. The impeller was inserted through the center port by means of a Chesapeake stirrer connection. Generally, the experiments were made at 0.2 percent solids, 90°C. For most of the tests, 325x400 mesh (d_{50} = 38 μm) particles were used. Solution samples, about 5 ml, were withdrawn through the fritted glass sampling device at selected time intervals and analyzed for copper concentration with a Perkin-Elmer model 305 atomic absorption spectrophotometer.

Surface morphology of the various products obtained before and after the leaching reaction was determined by the scanning electron microscope or the scanning transmission electron microscope with x-ray fluorescence for chemical analysis using nuclear diodes for energy dispersive analysis.

Reaction rates were determined from the data by fitting the experimental data to a polynomial regression equation. Similarly, the reaction parameters were deduced by a best fit statistical analysis of the rate data.

Electrical Conductivity Measurements. To determine the conductivity of C/S composites, carbon and sulfur of 99.98% purity were mixed and pressed into pellets. The size of the pellets was 1.27 cm in diameter and 0.19 cm thick. A wire-wound resistance furnace connected to a temperature controller was used for the conductivity measurement. A three-point electrode system was used to prevent surface leakage.[12] Bulk conductivities were measured under a helium atmosphere. Various types of carbon were first cleaned by heat treatment at 1373 K (1100°C) in flowing purified helium whose oxygen potential was less than 10^{-40} atmospheres. Such treatment cleanses the surfaces of the carbon

particles of absorbed species such as oxygen and hydrogen. The time necessary to obtain a steady conductivity value at a given temperature was rather long -- about two days. All the conductivity measurements were made under a flowing purified helium atmosphere. A Keithley digital electrometer (type 616) and a General Radio 1608-A impedance bridge were utilized to obtain the resistance of the pellets.

Experimental Results

The anodic dissolution of chalcopyrite in acid ferric sulfate solution at 90°C occurs according to the following reaction forming elemental sulfur:

$$CuFeS_2 + 4Fe^{3+} = Cu^{2+} + 5Fe^{2+} + 2S^\circ \qquad (3)$$

The formation of a dense and tenacious sulfur layer passivates the reaction and slows the leaching rate to unacceptably low levels. The addition of carbon particles reduces passivation and increases the leaching rate.

Significantly faster ferric sulfate leaching is achieved for $CuFeS_2$/C aggregates when compared to the results from the $CuFeS_2$ control experiment. The effects of carbon particles upon the rate of dissolution of chalcopyrite has been increased by 400% to 600% (after 10 hours' leaching) depending upon the carbon type, which varies in electrical conductivity and particle size.

The leaching characteristics of $CuFeS_2$/C aggregates are described from reaction rate experiments, conductivity measurements, and characterization of the elemental sulfur reaction product layer.

Particulate Carbon Properties

Nine different types of carbon have been evaluated in leaching studies and electrical conductivity measurements. The carbon types studied were Pearl 2000, Monarch 800, Monarch 1100, Fisher 38, Lonza KS-2.5, Spheron 6, Cerac

Pure Carbon, AESAR Graphite Fiber, and Activated Carbon. The particle size measurements, surface area measurements and DBT oil absorption measurements for these carbons are listed in Table 3. Particle sizes reported in this table are based on Coulter Counter measurements in our laboratory and also based on measurements from electromicrographs provided by the manufacturers. It seems that the former size is a measure of carbon aggregates which can become dispersed depending on the chemical environment. For example, the C/S composites exhibit good dispersion characteristics. The extent of dispersion of carbon in liquid sulfur is so great that individual carbon particles are difficult to identify even by Scanning Electronic Microscopy at a magnification of 4000.

Since particle size varies inversely with surface area, surface area measurements are used as an indirect measure of particulate carbon particle size. The size and complexity of the primary aggregates of the particulate carbon is referred to as the structure, and the structure level is measured by its oil absorption. Higher structure grades, which have a large void area, absorb more oil than lower structure grades with less void area. Both the particle size and the structure level properties affect the interaggregate distance for a given carbon loading in the sulfur system. C/S composites prepared with Black Pearl 2000 (the smallest particle size and highest structure level) had the highest electrical conductivity (Table 1). Generally, higher conductivity is achieved for carbons of smallest particle size. Also the conductivity of the C/S composites is strongly dependent of the amount of carbon used.

Table 3. Carbon Properties and Conductivities of C/S Composites

Carbon Type	Particle size (μm) Size Reported by Manufacturer	Particle size (μm) Coulter Counter d_{50}	Surface area m^2/g	σ_1* 5% C/S Composite $(ohm-cm)^{-1}$	σ_2* 15.9% C/S Composite $(ohm-cm)^{-1}$	DBT oil absorption cc/100 gm
Pearl 2000	15 nm	-	1348	2.6×10^{-2}	2.2×10^{-1}	330
Monarch 800	17 nm	2.1 μm	237.9	1.05×10^{-3}	-	75
Monarch 1100	14 nm	2.25 μm	258.8	9.0×10^{-4}	-	65
Lonza KS-2.5	<5 μm	4.3 μm	24.6	5.4×10^{-4}	1.6×10^{-1}	-
Spheron 6	25 nm	7.9 μm	11.9	2.2×10^{-4}	-	96
Fisher 38		10 μm	20.4	-	6.2×10^{-2}	-
Cerac Pure	-	13 μm	3.5	-	9.1×10^{-2}	-
Calgon Activated Carbon	-	4.3 μm		-	2.4×10^{-3}	-
AESAR Graphite Fiber	Dia. 8 μm Length 0.64 cm			-	-	
				Conductivity $(ohm-cm)^{-1}$		
Chalcopyrite (no carbon addition)				$\sim10^{+1}$		
Pure Sulfur				$\sim10^{-13}$		

*σ_1 and σ_2 are measured at 5 vol. % and 15.92 vol. % carbon in pure sulfur at 90°C, respectively.

Electrical Conductivity of Carbon/Sulfur Composites

From previous study, it appears that the leaching kinetics of chalcopyrite in ferric sulfate solution is limited by electron transport through the sulfur product layer. The electrical conductivity of the elemental sulfur product layer as estimated from the leaching response of chalcopyrite particles,[1] $t_e\sigma = 7.6\times10^{-13}$ $(ohm-cm)^{-1}$, compares favorably with the electrical

conductivity of pure crystalline orthorhombic sulfur at 90°C, $t_e\sigma = 10^{-13}$ $(ohm\text{-}cm)^{-1}$, reported in the literature.[14] As noted previously, the electrical conductivity of an insulator phase may well be increased by the addition of dispersed particles imbedded in the insulator phase. The change in conductivity of the matrix material is due to the emission of electrons from the dispersed particles into the insulating matrix phase.

A substantial increase in electrical conductivity has been found for the carbon-sulfur composite system compared to that of pure sulfur. The electrical conductivity data for different types of carbon dispersed in sulfur are listed in Table 3 and are plotted as a function of temperature in Figure 2.

The electrical conductivity of C/S composites significantly increases with an increase in the volume percent of carbon as shown in Figure 3. The addition of very small amounts of carbon (for example, 1.5 vol. % Black Pearl 2000) to sulfur increases the electrical conductivity by a factor of 10^{10} compared to pure sulfur.

The carbon particles embedded in the sulfur may serve as a source for electrons; if the concentration of electrons or holes in the sulfur matrix phase is low in comparison to those "given off" by the particles, then the electrical conductivity of the two-phase mixture may be determined primarily by the concentration of carriers emitted by the particles. However, if the volume fraction of dispersed conducting phase is high enough in an insulating matrix, then a continuous network of the highly conducting dispersed phase is expected to form, resulting in a high conductivity. Under these circumstances, the conductivity of the composite will not change significantly with the amount of carbon added.

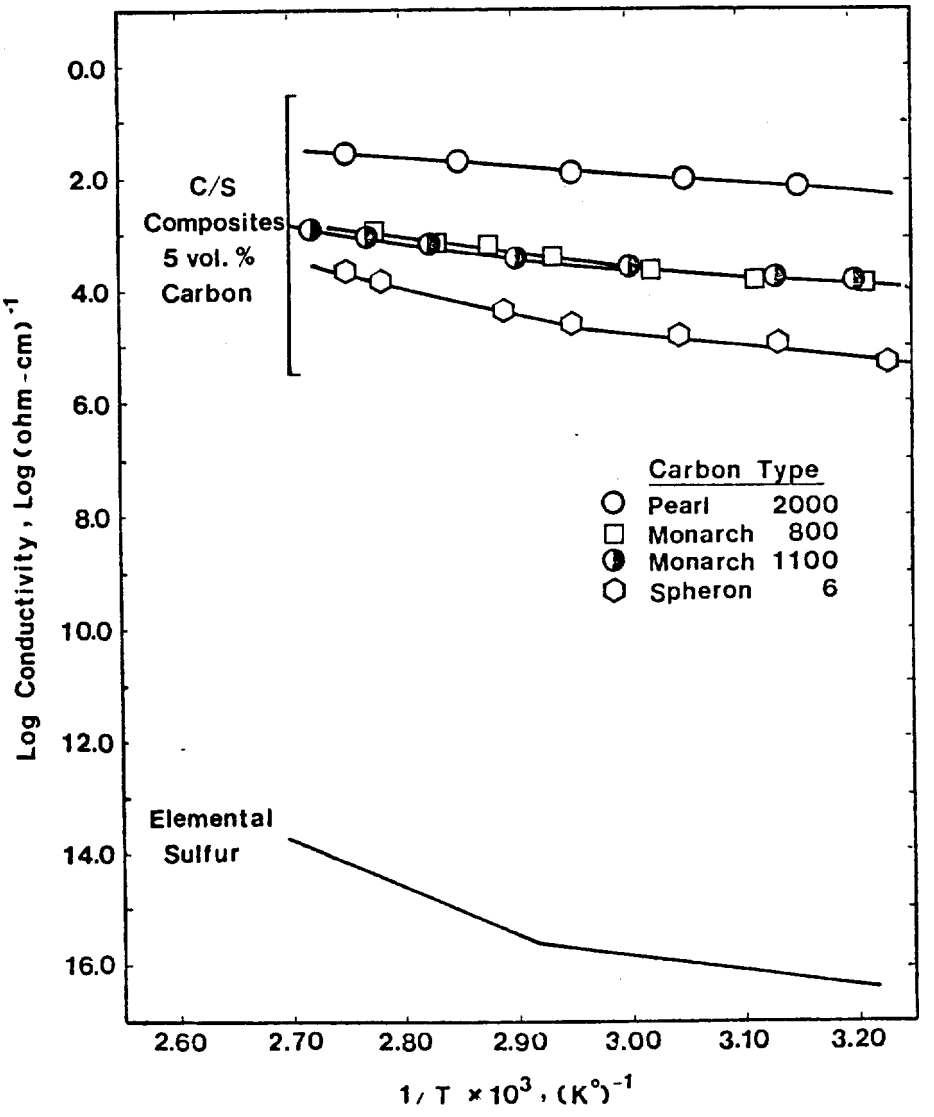

Figure 2. Electrical conductivities for different types of carbon added to pure sulfur as a function of temperature.

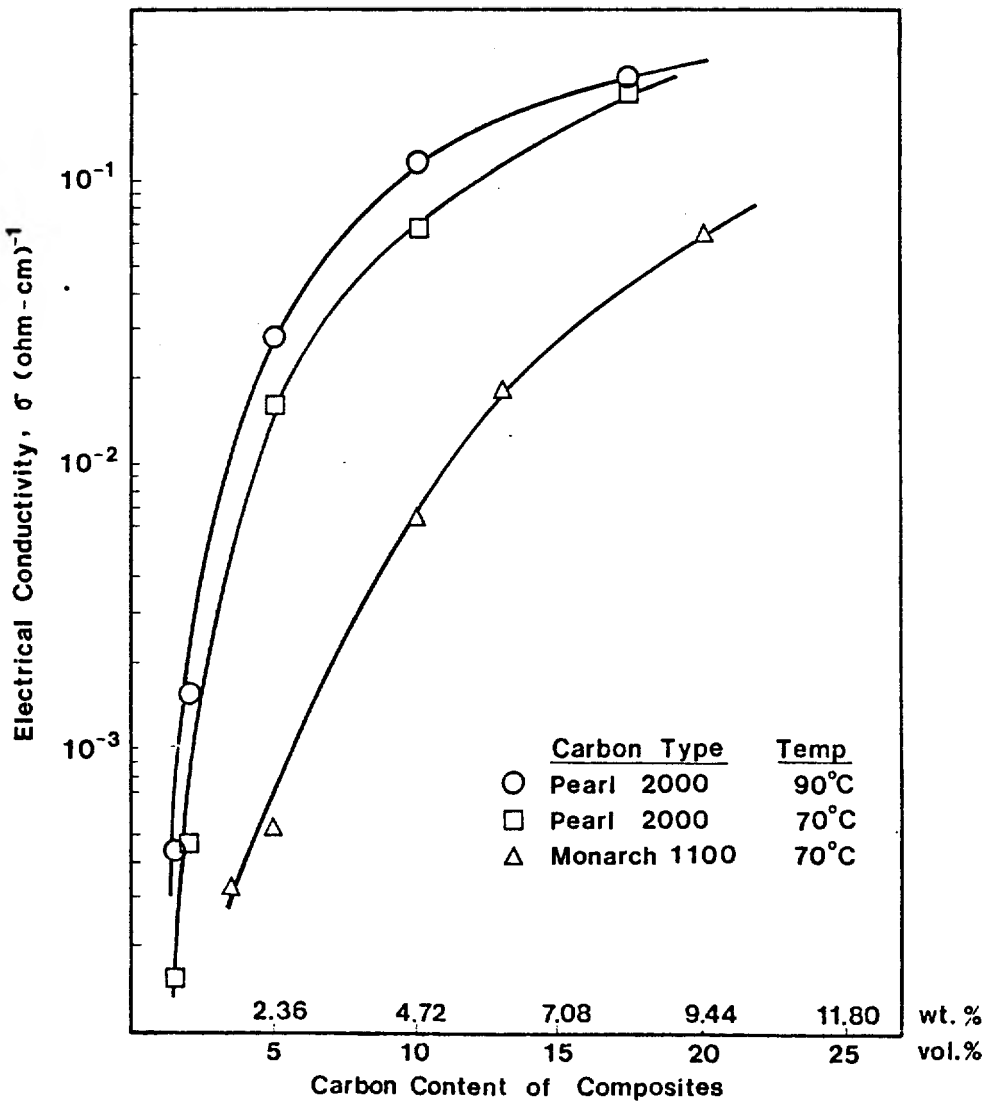

Figure 3. Electrical conductivities of C/S composites for different amounts of carbn addition.

Ferric Sulfate Leaching of $CuFeS_2$/C Aggregates

Significantly faster ferric sulfate leaching kinetics are achieved for $CuFeS_2$/C particulate aggregates than for suspended $CuFeS_2$ particles without carbon addition. The rate of ferric sulfate leaching of $CuFeS_2$/C aggregates at low stirring speed is much greater than the rate of leaching of suspended chalcopyrite particles at high speed (Figure 4). In fact, high stirring speeds for aggregate leaching appear to disrupt the $CuFeS_2$/C aggregates and the extent of reaction is reduced. The nature of the elemental sulfur product layer in the case of aggregate leaching differs significantly from the sulfur structure that forms in the absence of carbon.

Nine different types of carbon described above have been evaluated for the leaching of 38-μm chalcopyrite/carbon aggregates at 1 M H_2SO_4, 0.25 M $Fe_2(SO_4)_3$, 0.2% solids and 90-100 rpm. Among these carbons, Pearl 2000, which has the smallest particle size and the highest electrical conductivity for C/S composites, increases the leaching kinetics to the greatest extent, as shown in Figure 5. Interestingly, when the carbon content is reduced, even to 2% by weight, the leaching rate does not change.[13] The attached carbon particles accelerate the chalcopyrite leaching rate, which may be explained in part by the improved transport of electrons through the sulfur reaction product layer. The increase in the copper dissolution rate with respect to carbon type correlates to an increase in the electrical conductivity of the corresponding C/S composites as found from electrical conductivity measurement shown in Figure 6. Generally, high conductivity of C/S composites is achieved from the carbon of smallest particle size. It seems that the electrical conductivity of C/S composites is dependent upon the carbon particle size; however, the relationship is mainly due to the number of carbon particles dispersed in the composites. Modification of free sulfur reaction layer to increase the leach-

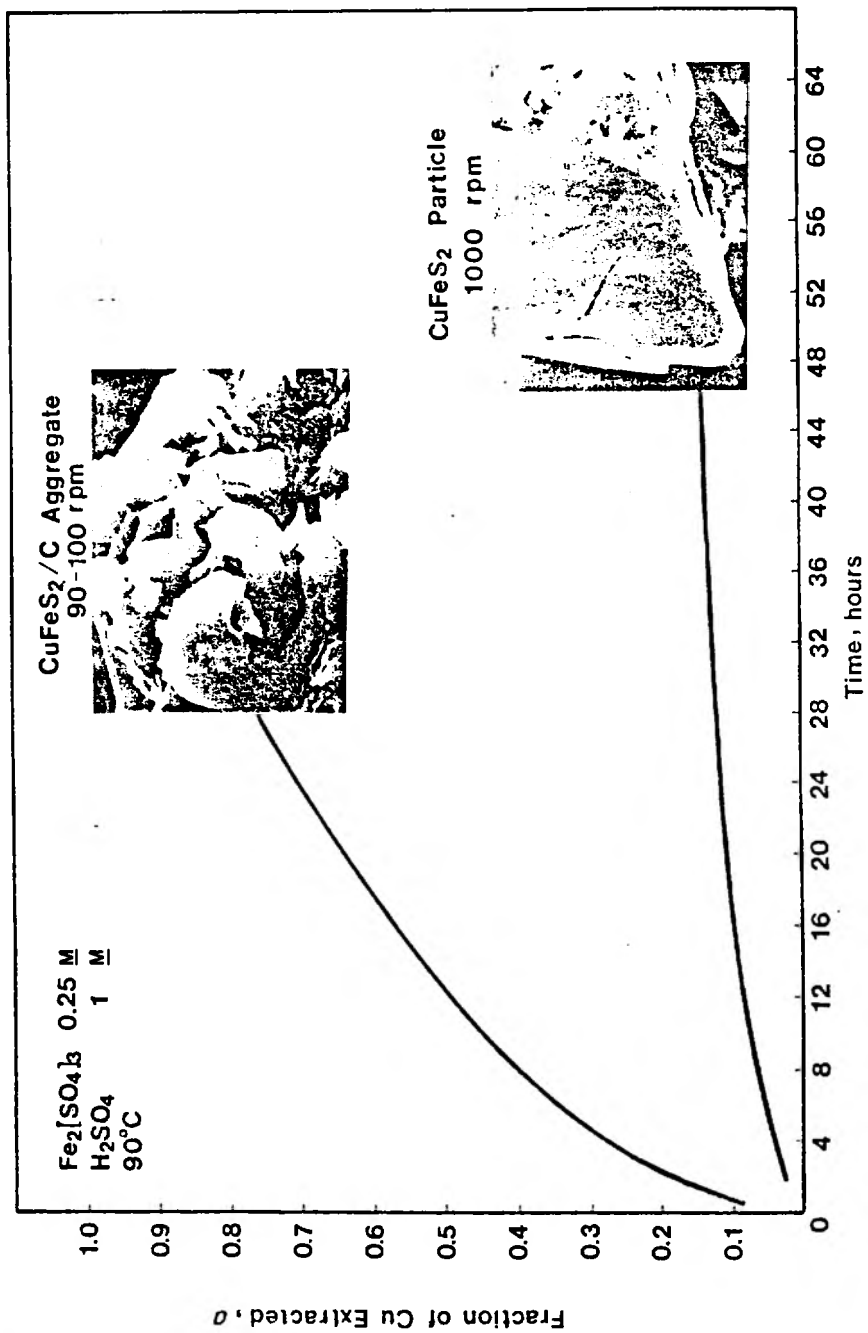

Figure 4. Comparison of the reaction rate of $CuFeS_2/C$ aggregates to the rate of suspended $CuFeS_2$ particles, d_o = 38 μm.

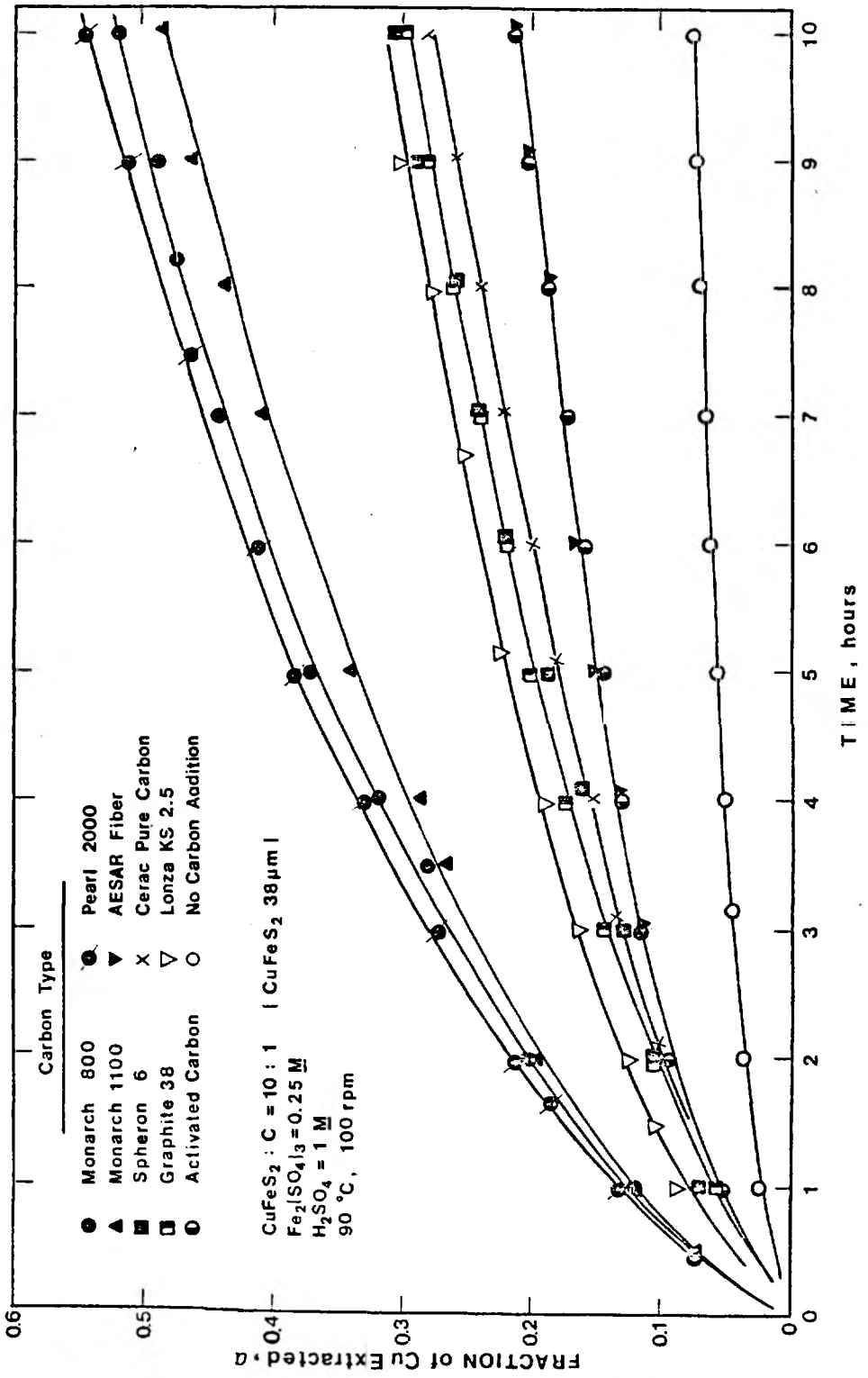

Figure 5. Fraction of Cu extracted from $CuFeS_2$/C aggregates prepared with different carbon types.

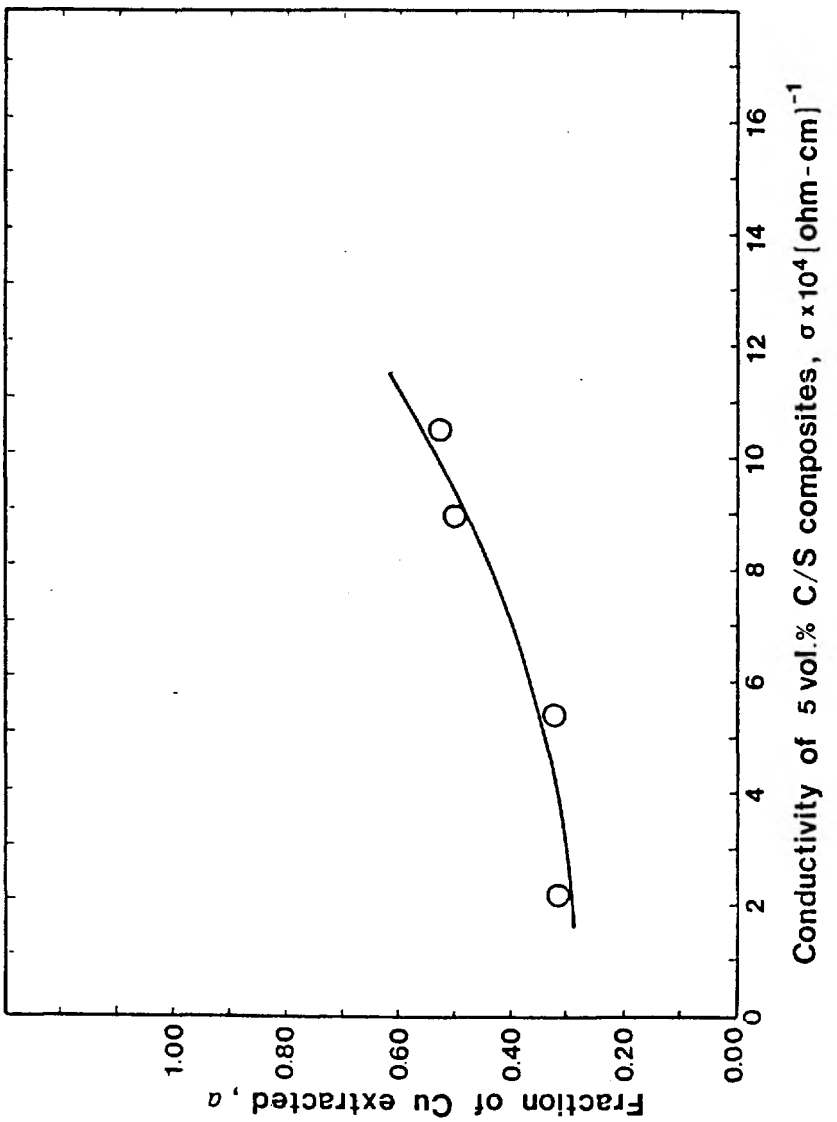

Figure 6. The relationship between fraction of Cu extracted from $CuFeS_2$/C aggregates for different carbon types and the electrical conductivity of the corresponding C/S composites.

ing rate depends on enhancement of the transport of electrons through the sulfur layer. In Figure 7, compare the leaching results obtained for $CuFeS_2$/Lonza KS-2.5 and $CuFeS_2$/activated carbon aggregates which have the same carbon size. $CuFeS_2$/Lonza KS-2.5 aggregates appeared to react faster than $CuFeS_2$/activated carbon. The sulfur composites prepared with Lanza KS-2.5 carbon also have greater electrical conductivity than the composites prepared with activated carbon.

The leaching results of 4.6- and 38-micron chalcopyrite particles and aggregates of these chalcopyrite samples prepared with carbon addition are compared in Figure 8 in terms of fraction reacted vs. time. For chalcopyrite particles without carbon, the rapid decreases in leaching rate with time is similar to that observed by other investigators; the tenacious sulfur layer on the chalcopyrite surface passivates the reaction. The beneficial effect of carbon addition seems to be more pronounced for coarse chalcopyrite particles, probably due to the breakage of these $CuFeS_2$ particles during compaction of the aggregate pellet. The particle size distributions of the chalcopyrite before and after compaction of the aggregate were determined with a Micromeritics Sedigraph Size Analyzer. The breakage of chalcopyrite particles during compaction of the aggregate is significant for the coarse $CuFeS_2$ but not for the finer $CuFeS_2$. In addition, it is interesting to note that the increased leaching rate is achieved at lower agitation speeds, presumably an indication the aggregate integrity must be preserved. The importance of compaction between carbon and chalcoprite particles is proved by the experimental results shown in Figure 9. Although the leaching rate of the mixed agglomerates of chalcopyrite and carbon particles (without pressing) is enhanced, yet it is not as high as the compressed $CuFeS_2$/C pellets mentioned before.

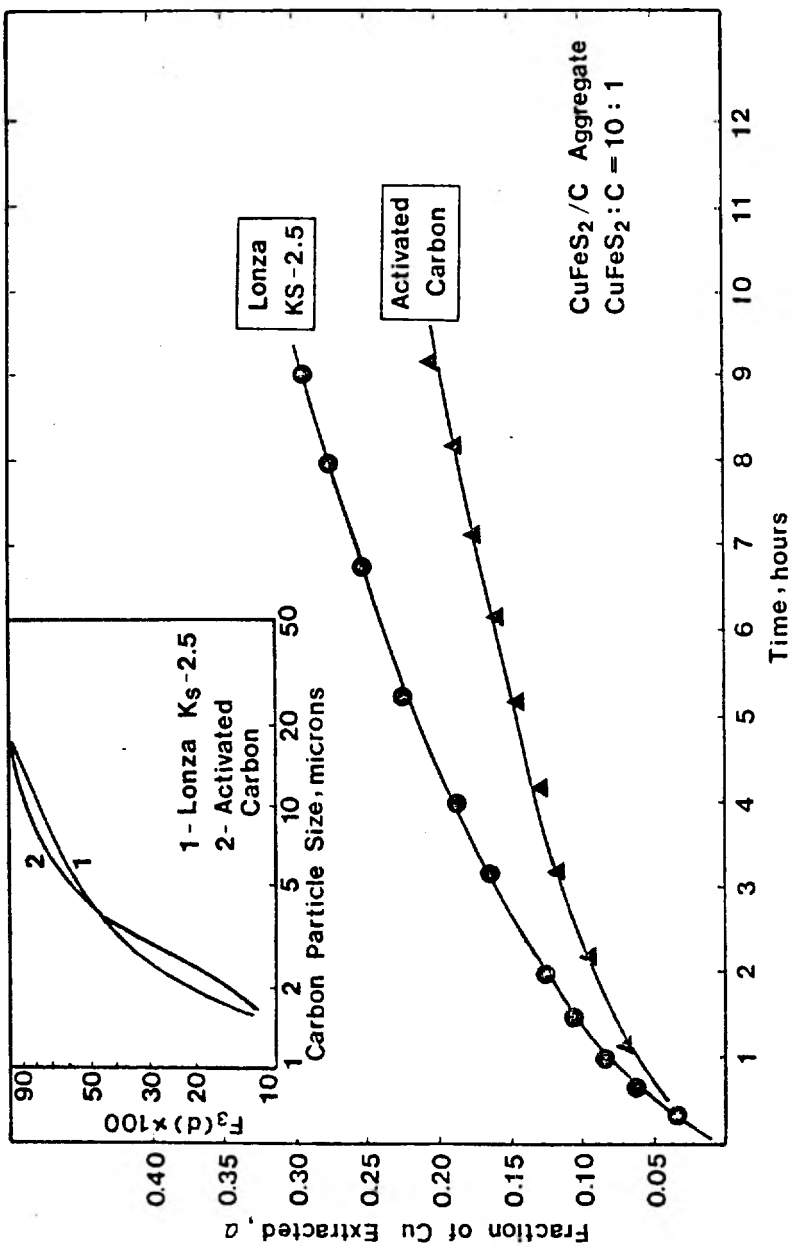

Figure 7. Fraction of Cu extracted from chalcopyrite as $CuFeS_2$/C aggregates for Lanza KS-2.5 and activated carbon. $Fe_2(SO_4)_3$ 0.25 M, H_2SO_4 1 M, 90°C, 90-100 rpm, $d_{o\ CuFeS_2}$ = 38 μm.

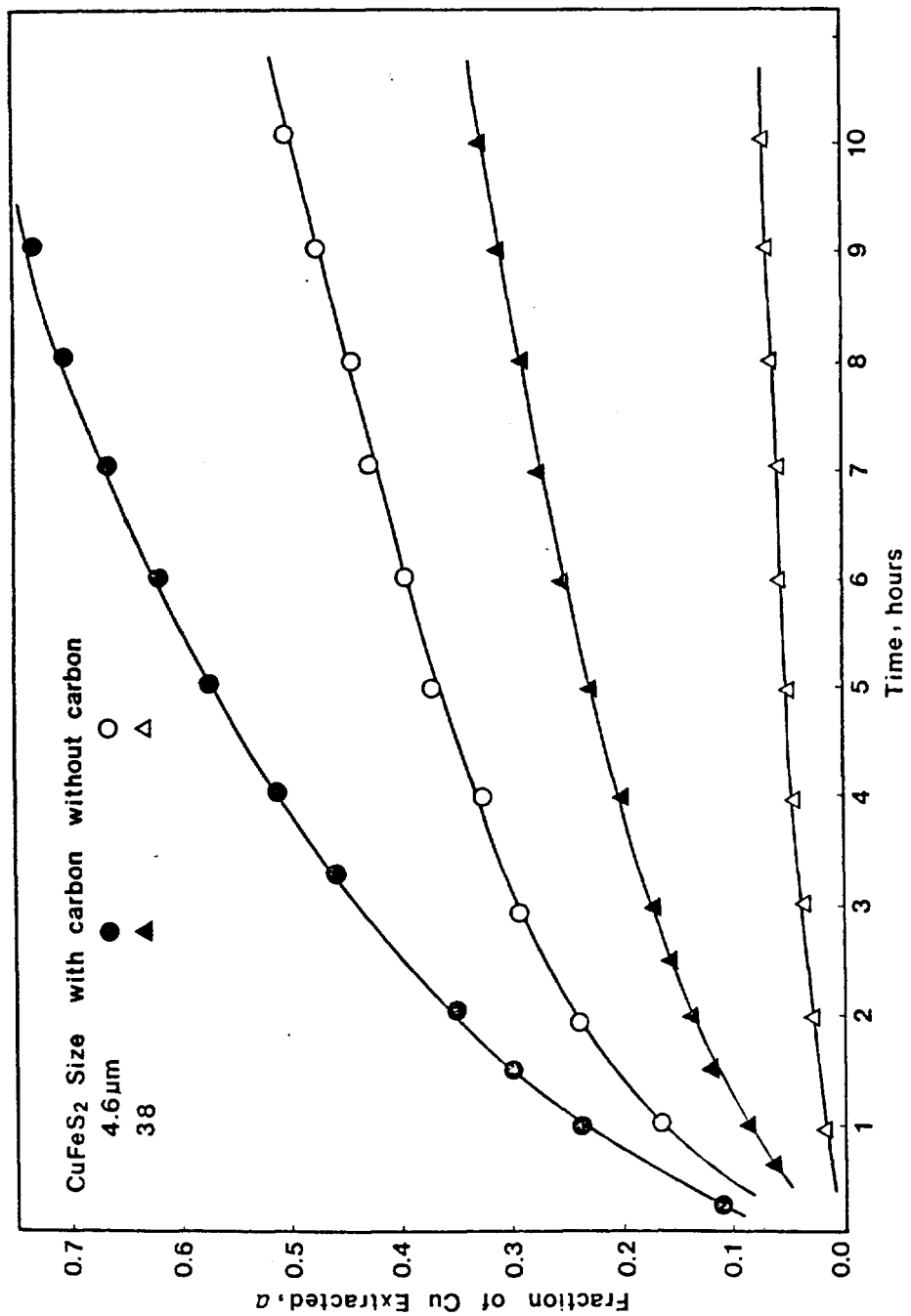

Figure 8. Fraction of Cu extracted from chalcopyrite in an acid ferric sulfate solution as suspended $CuFeS_2$ particles and as $CuFeS_2$/C aggregates for different $CuFeS_2$ particle sizes. $Fe_2(SO_4)_3$ 0.25 M, H_2SO_4 1 M, 90°C, $CuFeS_2$:Fisher 38 carbon = 10:1.

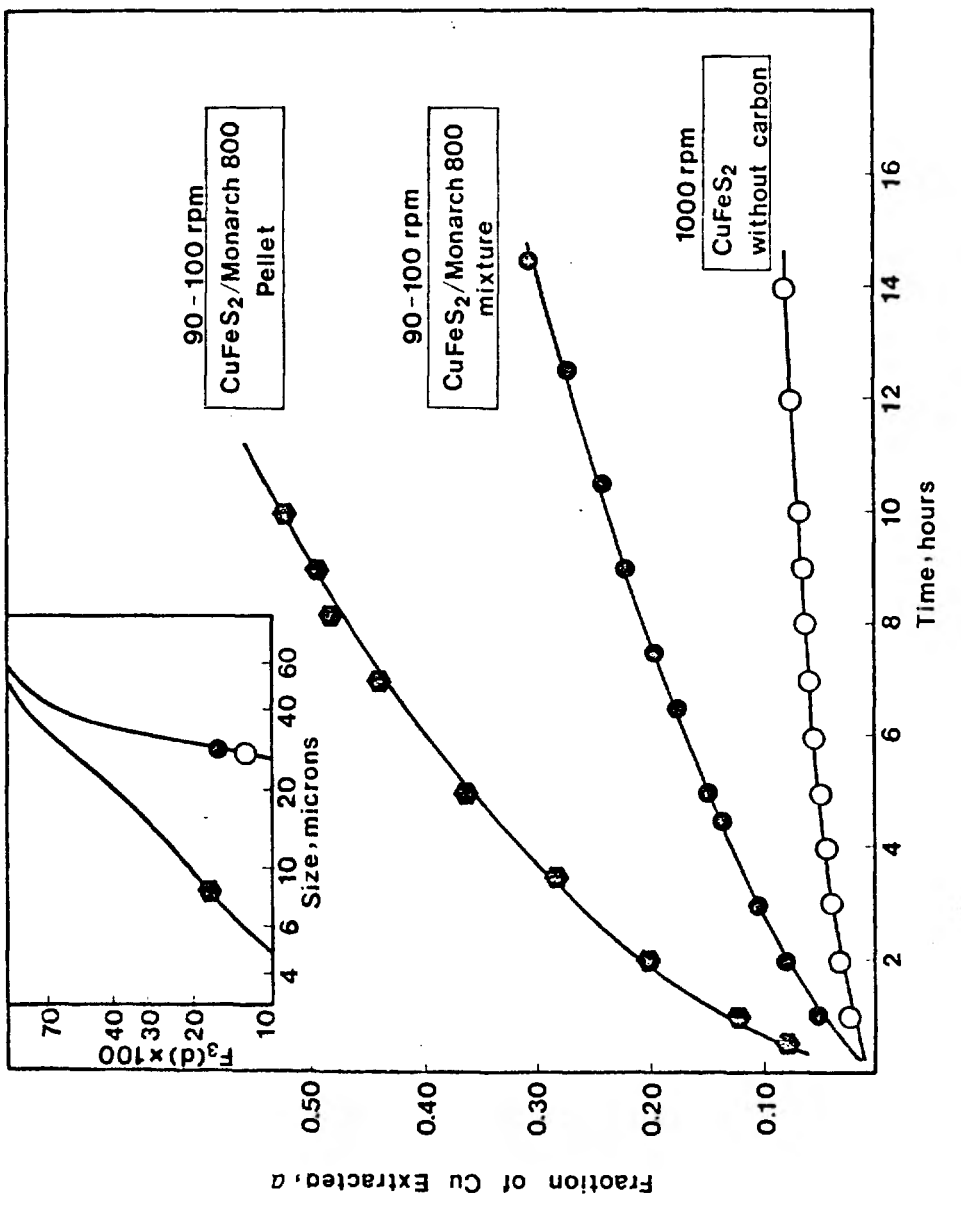

Figure 9. Fraction of Cu extracted from chalcopyrite as suspended $CuFeS_2$ particles and as $CuFeS_2$/C aggregates. $Fe_2(SO_4)_3$ 0.25 M, H_2SO_4 1 M, 90°C, $CuFeS_2$:C = 10:1.

Wetting Characteristics of Elemental Sulfur

As shown in Figures 10 and 11, the morphology of the elemental sulfur formed during the leaching of chalcopyrite/carbon aggregates differs significantly from the dense, tenacious sulfur layer which forms on the $CuFeS_2$ surface in the absence of carbon. The sulfur product formed from $CuFeS_2$/C aggregates has been found to have a more botryoidal, less protective character. The inability to identify carbon particles by microscopic examination of C/S composites suggests that excellent dispersion of carrbon agglomerates occurs in liquid sulfur. The carbon particles at the chalcopyrite surface may act as nuclei for sulfur growth during the leaching reaction and contribute to the nonuniform, less protective nature of the product layer. In this regard, the wetting of carbon and chalcopyrite by liquid sulfur has been studied to aid in the characterization of the reaction product.

Wetting, in this study, is described by the contact angle measured through the liquid drop at the surface. Small values of the contact angle would be indicative of better wetting characteristics. Nonwetting would be indicated by large contact angle. Wetting signifies an adhesion of the liquid phase to the surface so that the cohesion of the spreading (wetting) phase is exceeded. Theoretically, for liquid (ℓ) at a solid surface (s), spreading of the liquid will occur if the spreading coefficient is greater than zero:

$$S = \gamma_{\ell} - \gamma_s - \gamma_{\ell/s} > 0 \qquad (4)$$

where γ_{ℓ}, γ_s, and $\gamma_{\ell/s}$ are the surface tensions of the spreading liquid phase, the solid surface and the liquid/solid interface respectively. A force balance in the horizontal direction gives the Young equation:

$$\gamma_{\ell} = \gamma_s + \gamma_{\ell/s} \cos \theta \qquad (5)$$

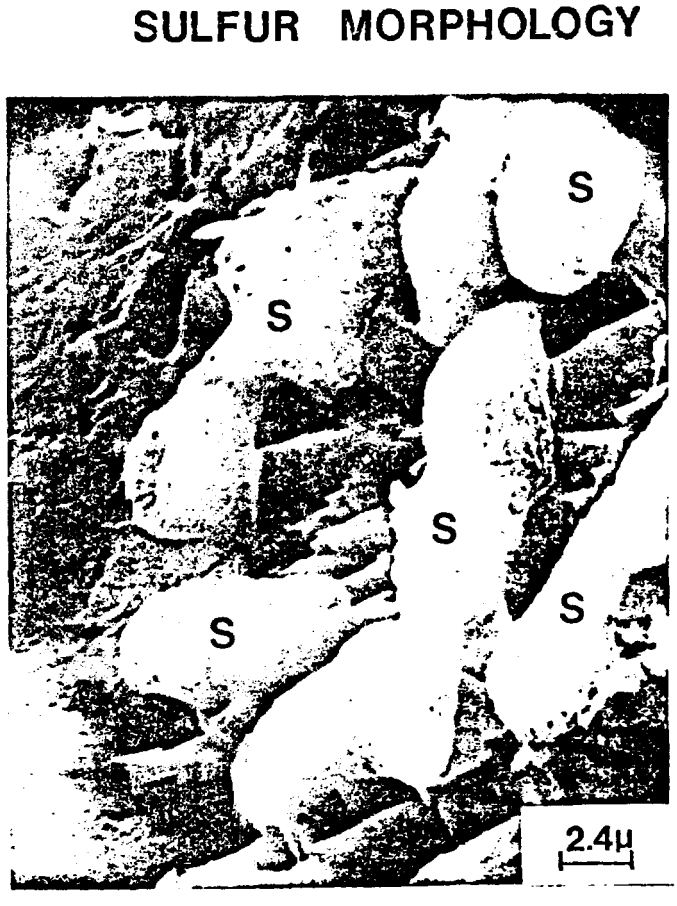

Figure 10. SEM photomicrograph of partially leached chalcopyrite/carbon aggregate by ferric sulfate solution. d_o 38 μm, α = 0.40.

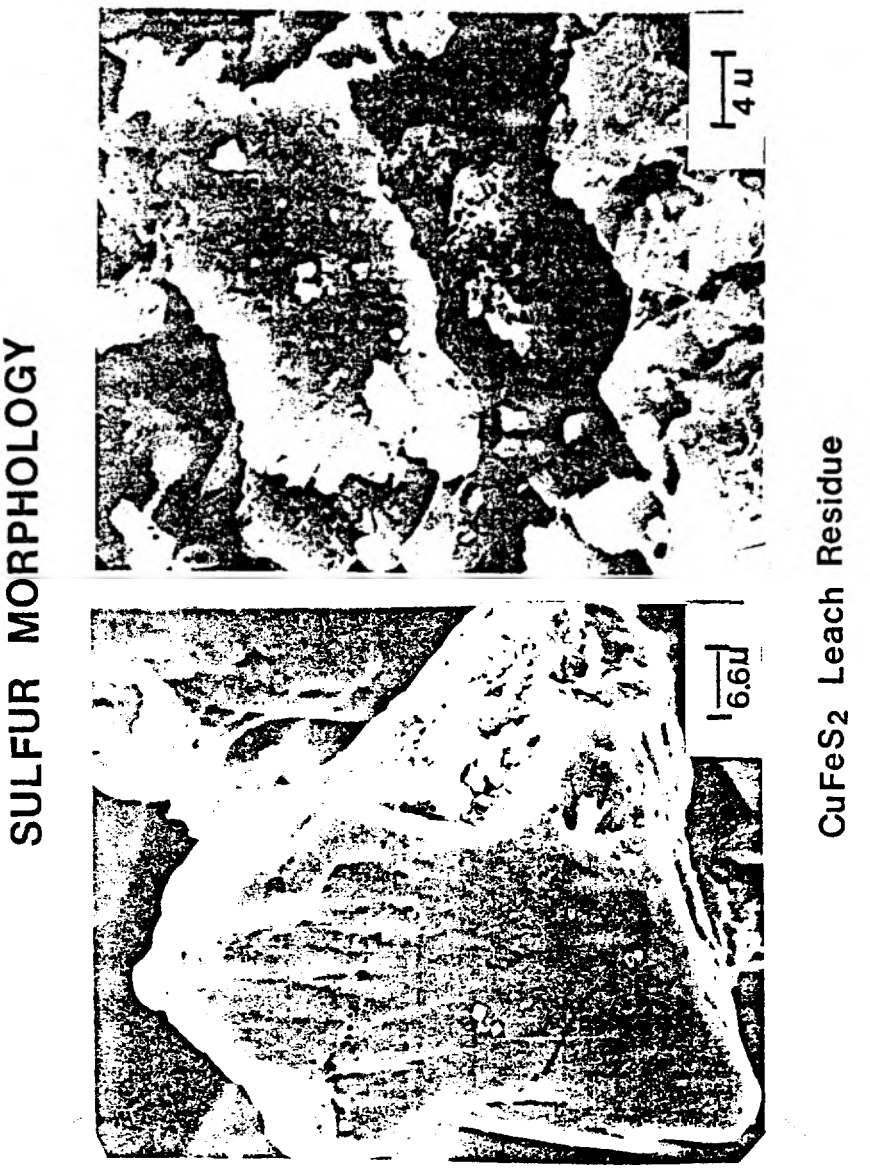

Figure 11. SEM photomicrograph of partially leached chalcopyrite particle by ferric sulfate solution. (A) d_o 38 μm, α = 0.17; (B) d_o 12 μm, α = 0.20.

From which the spreading coefficient for wetting would be

$$S = \gamma_{\ell/s} (\cos \theta - 1) > 0 \qquad (6)$$

In this study, contact-angle measurements were carried out above the melting point of elemental sulfur, and a N_2 protective atmosphere was used to prevent air oxidation. The solid surface was polished and treated by a Plasmod system to clean the solid surface of absorbed species. To measure the sulfur wetting characteristics, several samples were selected, including chalcopyrite, pyrite, quartz, talc, gold, and graphite. The contact angles measured between the liquid sulfur and the solid surfaces are presented in Figure 12.

These experiments demonstrate that elemental sulfur tends to completely wet a carbon surface as well as a gold surface. Somewhat surprisingly, such is not the case for a chalcopyrite surface. It seems that the wetting of the carbon particles by the elemental sulfur reaction product is an important factor which ensures good dispersion characteristics. These results are consistent with those regarding the dispersion of carbon particles in elemental sulfur. The extent of dispersion of carbon in liquid sulfur is so great that individual carbon particles are difficult to identify even with the scanning electron microscope.

However, it seems that this wetting property is of secondary importance compared to electrical conductivity. For example, it has been found that aggregates of chalcopyrite compacted with nonconductive particles such as talc, silica, or alumina did not result in enhanced reaction rates.

The wetting characteristics of sulfur suggest that excellent dispersion of carbon agglomerates occurs in liquid sulfur. It is thought that this phenomena may occur to a small extent at the chalcopyrite interface during ferric

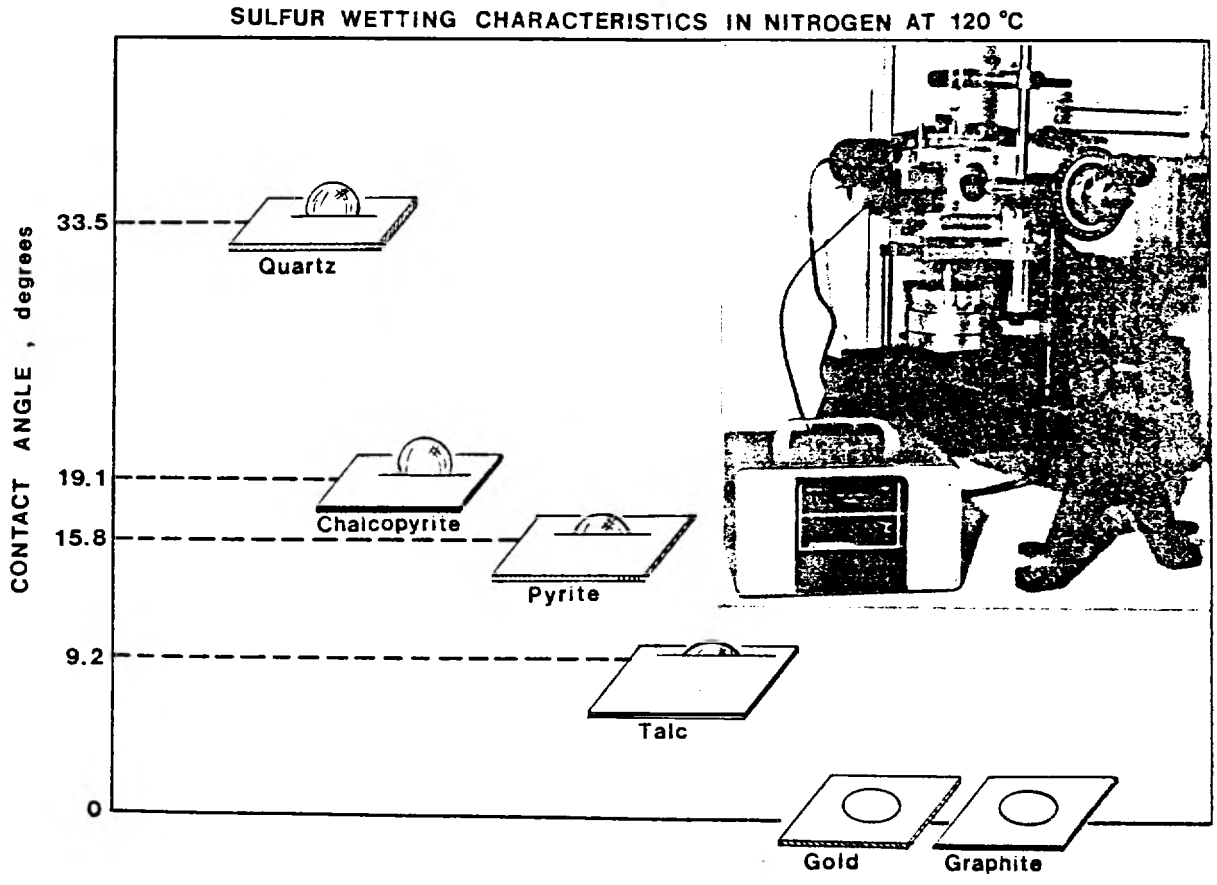

Figure 12. Contact angles between the liquid sulfur and the solid surfaces.

sulfate leaching at 90°C. The conductive particles may improve the electrical conductivity of the sulfur product layer and lead to enhance the reaction rate. As would be expected aggregates prepared with gold and platinum particles exhibit enhanced leaching rates.

Discussion of Reaction Mechanism

The experimental results show that enhanced reaction kinetics in the ferric sulfate leaching of $CuFeS_2$/C aggregates can be expected under certain circumstances. But the kinetic aspects of this reaction are complicated, more than one rate process may be involved. The reaction mechanism will be discussed in etail in another publication.[14] A reaction mechanism summary follows.

For the ferric sulfate leaching reaction of chalcopyrite, it seems that the reaction rate is limited by the transport of electrons through the protective sulfur product layer. The very slow parabolic reaction kinetics were predicted using Wagner's theory of oxidation, which relates the electrical conductivity of the elemental sulfur reaction product to the rate of reaction. For the $CuFeS_2$/C aggregates, the reaction kinetics may involve both surface reaction and product layer transport. Since the sulfur layer is not of uniform thickness in the leaching of $CuFeS_2$/C aggregates, short transport paths may allow electrochemical processes to become significant and limit the rate during the early stages of reaction. Also the addition of carbon particles alters the sulfur structure and facilitates electron transport through the sulfur product layer. The provision for a surface reaction seems necessary, and the rate data can be analyzed with a mixed kinetics rate expression involving both surface reaction and product layer transport.

The parabolic rate constant which involves the conductivity of the sulfur layer has been compared to the electrical conductivity of C/S composites. The

fact that the parabolic reaction rate constant of $CuFeS_2$/C aggregates with different types of carbon increases with an increase of electrical conductivity of the corresponding C/S composites (shown in Figure 13) supports the proposed reaction mechanisms.

Further support for this reaction mechanism is given by the temperature dependence of the $CuFeS_2$/C leaching data. Very high activation energies of 27.5 kcal/mole (115.1 kJ/mole) for $CuFeS_2$/Monarch 800 aggregates and 28.8 kcal/mole (120.5 kJ/mole) for $CuFeS_2$/Spheron 6 aggregates were obtained for the parabolic rate constant (Figure 14). These observed activation energies are larger than normally would be expected for a transport process. However, they are consistent with what has been observed for the temperature coefficient of the conductivity C/S composites. The electrical conductivity for Spheron 6 carbon in C/S composites has been studied as a function of temperature (Figure 14). The value of the activation energy for electron transport in 5 vol. % Spheron 6 carbon in sulfur, 25.3 kcal/mole (105.9 kJ/mole), is very close to the experimental activation energy in the ferric sulfate leaching of chalcopyrite. There is a trend that the activation energy decreases as the volume percent carbon in the C/S composites increases. In fact recent evidence indicates that the activation energy for electron transport in C/S composites can exceed 40 kcal/ mole depending on composition.

Conclusions

1. The ferric sulfate leaching of chalcopyrite particles is affected by the ~~nature of~~ tenacious sulfur product layer formed, and ~~the~~ dissolution rates are extremely slow. The reaction kinetics can be improved by the addition (2% by weight) of ~~conductive~~ conductive particles such as carbon to form an aggregate which leaches ~~significantly~~ faster than individual chalcopyrite particles. The ~~ferric sulfate leaching of chalcopyrite with the~~ addition of carbon

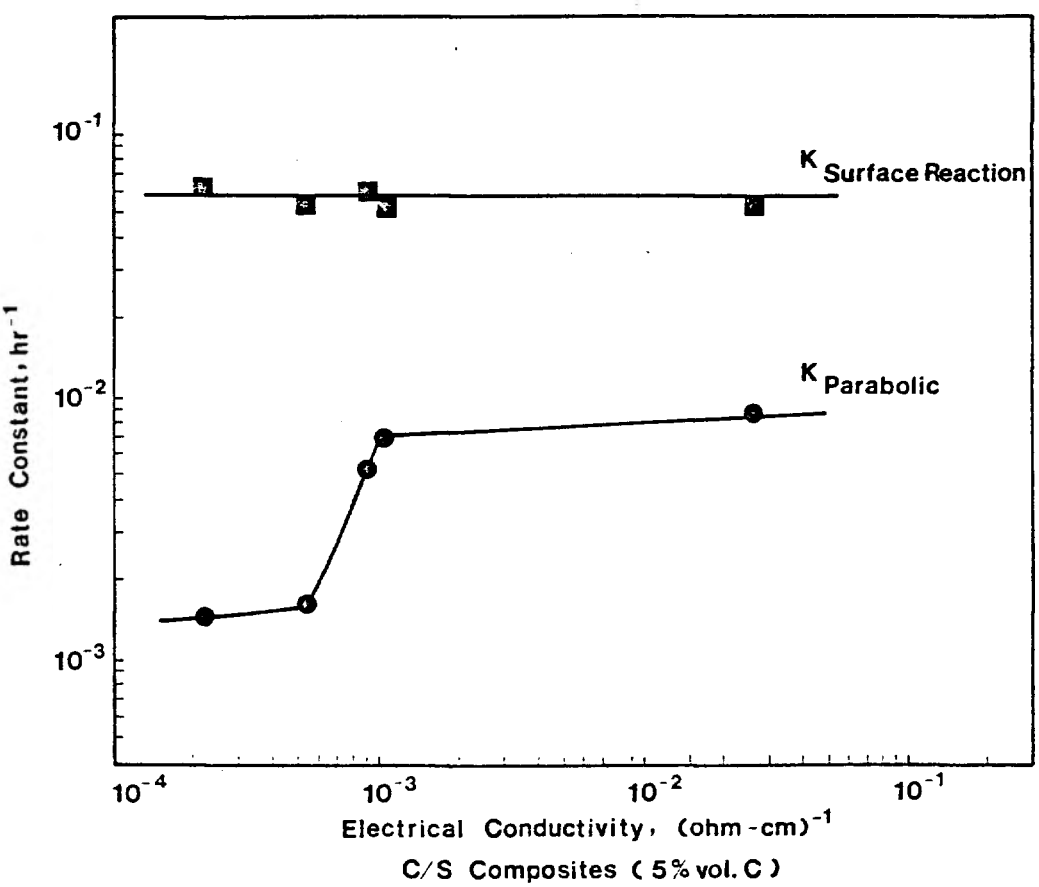

Figure 13. Leaching reaction rate constants of $CuFeS_2/C$ aggregates with different types of carbon vs. electrical conductivities of the corresponding C/S composites.

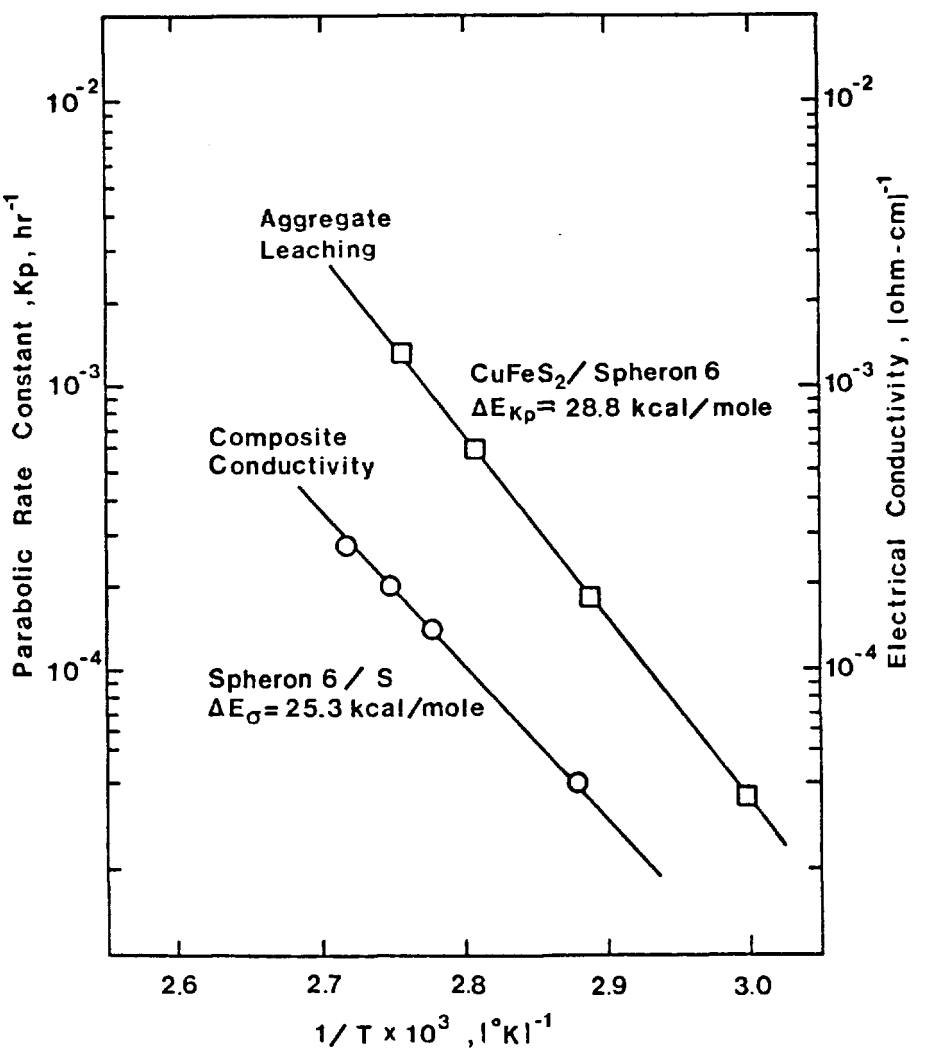

Figure 14. Arrhenius plots: (1) Parabolic reaction rate constant, k_p vs. inverse absolute temperature for $CuFeS_2$/Spheron 6 carbon aggregates. (2) Electrical conductivity vs. inverse absolute temperature for Spheron 6 carbon/S composites.

(2)

particles ~~has been found to~~ increase the reaction rate by 400-600% (after 10 hours' leaching) depending upon the carbon type, which varies in electrical conductivity and ~~carbon~~ particle size.

2. The electrical conductivity measurements have demonstrated that the addition of carbon to solid sulfur increases the sulfur conductivity substantially by 10 orders of magnitude. The increase in leaching rate of the $CuFeS_2/C$ aggregates may be explained for the most part by the improved transport of electrons through the sulfur reaction product layer. The parabolic rate constant calculated from the leaching data for $CuFeS_2/C$ aggregates with different types of carbon increases with increase in electrical conductivity of the corresponding C/S composite.

(3)

3. The temperature dependence of $CuFeS_2/C$ aggregate leaching reaction gives a high activation energy of 27.5 kcal/mole (115.1 kJ/mole). The observed activation energy is larger than normally would be expected for a transport process but is close to the activation energy calculated from the temperature coefficient for the electrical conductivity of carbon/sulfur composites.

4. The sulfur product formed from $CuFeS_2/C$ aggregates has been found to have a more botryoidal, less protective character. The carbon particles at the chalcopyrite surface may act as nuclei for sulfur growth during the leaching reaction and contribute to the nonuniform, less protective nature of the product layer. The wetting of the carbon particles by elemental sulfur may also be an important factor in the increased leaching rate. The elemental sulfur was found to wet a carbon surface, while a definite contact angle was developed at a chalcopyrite surface.

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